

## Chem 30A Spring 2005

MIDTERM \#2
(50 Min)

Weds May 25th

INTERPRETATION OF THE QUESTIONS IS PART OF THE EXAM DO NOT ASK FOR THE QUESTIONS TO BE EXPLAINED TO YOU

ONLY ANSWERS WRITTEN IN THE BOXES PROVIDED WILL BE GRADED *** DO NOT OPEN THIS EXAM UNTIL INSTRUCTED TO DO SO***

| Q1 | $/ 26$ | Q4 | $/ 20$ |
| :---: | :---: | :---: | ---: |
| Q2 | $/ 12$ | Q5 (BONUS) | $/ 15$ |
| Q3 | $/ 42$ | Total | $/ 100$ |

"A scientific truth does not triumph by convincing its opponents and making them see the light, but rather because its opponents eventually die and a new generation grows up that is familiar with it."

- Max Planck
"It is disconcerting to reflect on the number of students we have flunked in chemistry for not knowing what we later found to be untrue."
- Robert L Weber

Q1. Each of the reactions drawn below produces ONE MAJOR PRODUCT. In each case, draw this product (including relative stereochemistry where appropriate) in the large box provided (3 points each). Note: for two-step reactions, just give the final product, DO NOT draw intermediates. If a reaction produces a mixture of stereoisomers, write an ' $\mathbf{S}$ ' in the small box next to it - be sure of your answer, +1 point for each correct ' $\mathbf{S}$ ' and -1 point for each incorrect ' $\mathbf{S}$ '.


Question 1 is continued on the next page...
(d)


(e)


$$
\xrightarrow[\mathrm{H}_{2} \mathrm{SO}_{4} \text { (cat) }]{\mathrm{H}_{2} \mathrm{~S}}
$$


(f)

(i) $\mathrm{Hg}(\mathrm{OAc})_{2} / \mathrm{MeOH}$ $\xrightarrow[\text { (ii) } \mathrm{NaBD}_{4}]{ }$
(g)

(i) $\mathrm{OsO}_{4}$
(ii) $\mathrm{NaHSO}_{3} / \mathrm{H}_{2} \mathrm{O}$


Q2. Propose a mechanism for the reaction shown in the box below (show all intermediates, all appropriate lone pairs, formal charges, and curly arrows). (12 pts)



Q3. (a) In the reaction between 1,2-dideuteriocyclopentene and ozone, the first step is a 1,3-dipolar cycloaddition between the two reactants to form a molozonide (A). The molozonide subsequently rearranges by first undergoing a reverse 1,3-dipolar cycloaddition, followed by another 1,3-dipolar cycloaddition, to form an ozonide (B). In the boxes below, draw the structures of $\mathbf{A}$ and $\mathbf{B}$ (in this part of the question, and all following parts, make sure to indicate the deuterium (D) atoms, paying particular attention to their relative stereochemistry). (6 pts)

(b) In the box below, propose a mechanism for the formation of the molozonide $\mathbf{A}$ (show all intermediates, all appropriate lone pairs, formal charges, and curly arrows). Comment, in a few words, on the stereospecificity (if any), of this initial 1,3-dipolar cycloaddition. (6 pts)
(c) In the box below, propose a mechanism for the rearrangement of the molozonide $\mathbf{A}$ into the ozonide B (show all intermediates, all appropriate lone pairs, formal charges, and curly arrows). (8 pts)
(d) Suggest a reason why the molozonide (A) rearranges into the ozonide (B) (i.e., why is the ozonide more stable than the molozonide?). (4 pts)
(e) In a second step, the ozonide (B) is decomposed upon treatment with dimethyl sulfide $\left(\mathrm{Me}_{2} \mathrm{~S}\right)$ to give the dialdehyde compound shown below (at the same time, the dimethyl sulfide is converted into dimethyl sulfoxide). In the box below, propose a mechanism for the reaction between $\mathbf{B}$ and $\mathrm{Me}_{2} \mathrm{~S}$ (show all intermediates, all appropriate lone pairs, formal charges, and curly arrows). (8 pts)

(f) 1,3-Dipolar cycloaddition reactions are not limited to alkenes and ozone; alkynes and azides also undergo such reactions to form compounds called triazoles. In the reaction shown below, benzyl azide reacts with 2-pentyne to form two constitutionally isomeric compounds $\mathbf{C}$ and $\mathbf{D}$, with the molecular formula $\mathrm{C}_{12} \mathrm{H}_{15} \mathrm{~N}_{3}$. Draw the structures of $\mathbf{C}$ and $\mathbf{D}$ in the boxes shown below (note: the labels $\mathbf{C}$ and $\mathbf{D}$ are arbitrary). (6 pts)

(g) In the box below, propose a mechanism for the 1,3-dipolar cycloaddition reaction between the alkyne and azide from the previous part of this question (show all intermediates, all appropriate lone pairs, formal charges, and curly arrows). (4 pts)

Q4. An optically active (chiral) compound $\mathbf{A}\left(\mathrm{C}_{10} \mathrm{H}_{16}\right)$ reacts with hydrogen in the presence of a Pt catalyst to give two diastereoisomeric compounds $\mathbf{B}$ and $\mathbf{C}$, each with the formula $\mathrm{C}_{10} \mathrm{H}_{20}$. Both $\mathbf{B}$ and $\mathbf{C}$ are optically inactive (achiral). When A undergoes an ozonolysis reaction $\left(\mathrm{O}_{3} / \mathrm{Me}_{2} \mathrm{~S}\right)$, two compounds are formed; the diketoaldehyde (D) shown below, and compound $\mathbf{E}$. Draw the structures of compounds $\mathbf{A}, \mathbf{B}, \mathbf{C}$, and $\mathbf{E}$, in the boxes at the bottom of this page, including any relevant stereochemistry. (20 pt)


Space for working...


Q5 (BONUS). For each transformation of 1-butyne shown below, suggest what deuterium labeled reagents will give rise to the indicated product as the MAJOR product in each case. For each reaction, the required number of steps is indicated by the number of boxes. ( 15 pt )
(a)


(b)

(ii)

(c)

(ii)

(d)

(ii)

(e)


(iii)

